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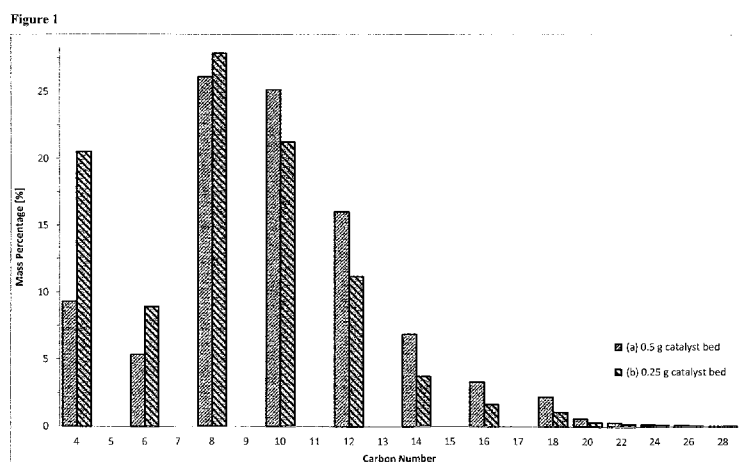
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(54) Title: PRODUCTION OF A LIQUID HEAVY HYDROCARBON COMPOSITION



(57) Abstract: A process for the preparation of a liquid heavy hydrocarbon composition from ethylene, wherein said process comprises the following steps: (a) feeding an ethylene composition in to an oligomerisation reaction zone containing a supported nickel oligomerisation catalyst to form an oligomerisation product A, wherein the oligomerisation reaction is operated at a temperature in the range of from 30 to 300 °C and a pressure of at least 10 bara; (b) separating a light products stream B, a middle distillate product stream C and a heavy products stream D from oligomerisation product A, wherein the light product stream B comprises the fraction of oligomerisation product A which boils in the C2-C8 mono-olefin boiling range, the middle distillate product stream C comprises a fraction of oligomerisation product A which boils above the boiling range of the light product stream B and below the boiling range of the heavy products stream D, and wherein the heavy product stream D comprises the fraction of oligomerisation product A which boils above the C22 mono-olefin boiling range; (c) recycling at least a portion of the light products stream B to the oligomerisation reaction zone of step (a) of the process; (d) optionally recycling at least a portion of the middle distillate product stream C to the oligomerisation reaction zone of step (a) of the process; and (e) hydrogenating the heavy products stream C, wherein the at least a portion of the hydrogenated heavy products stream D is recovered as the liquid heavy hydrocarbon composition.



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PRODUCTION OF A LIQUID HEAVY HYDROCARBON COMPOSITION

The present invention relates to the production of a liquid heavy hydrocarbon composition from ethylene, said process comprising the oligomerisation of ethylene, and wherein the liquid heavy hydrocarbon composition comprises paraffinic hydrocarbons which boil above the C22 mono-olefin boiling range. Also provided by the present invention is a process for the conversion of an ethanol composition into a liquid heavy hydrocarbon composition, said process comprising the dehydration of ethanol to ethylene and subsequent oligomerisation of the ethylene.

Several hydrocarbon based products contain or are liquid heavy hydrocarbon compositions; examples of such products include base oils, base stocks, lubricant compositions and fuel oils.

Lubricant compositions typically comprise a base oil and one or more additive; such additives being known in the art. Base oils typically comprise at least one base stock.

Base stocks may be defined as Group I, II, III, IV and V base stocks according to API standard 1509, "ENGINE OIL LICENSING AND CERTIFICATION SYSTEM", April 2007 version 16th edition Appendix E.

Liquid heavy hydrocarbon compositions are traditionally derived from crude oil in a refinery. Other sources of such liquid heavy hydrocarbon compositions include the Fischer-Tropsch process and dimerization, trimerisation and tetramerisation of linear alpha olefins having at least six carbon atoms.

WO 2010/066830 A1 discloses a process to make alpha olefins comprising: dehydrating ethanol to recover an ethylene stream, introducing said ethylene stream into an oligomerization zone containing an oligomerization catalyst and into contact with said oligomerization catalyst, operating said oligomerization zone at conditions effective to produce an effluent consisting essentially of 1-butene, 1-hexene, optionally heavier alpha olefins and unconverted ethylene if any, introducing the above effluent into a fractionation zone to recover a stream consisting essentially of 1-butene, a stream consisting essentially of 1-hexene, optionally a stream consisting essentially of heavier alpha olefins and an optional ethylene stream. In another embodiment of WO 2010/066830 A1, the 1-hexene or at least one heavier alpha olefins, if any, are isomerized to an internal olefin and subsequently transformed by metathesis with the aid of additional ethylene into different

alpha-olefins with even or odd number of carbons. By way of example, 1-hexene is isomerized into 2-hexene and by methathesis with ethylene converted to 1-pentene and propylene. In another embodiment of WO 2010/066830 A1, the oligomerization zone is only a dimerization zone and butene is produced. 1-butene is isomerized to 2-butene and sent to a methathesis zone in the presence of ethylene to be converted to propylene. In said embodiment the dehydration catalyst is selected in the group consisting of a crystalline silicate having a ratio Si/Al of at least about 100, a dealuminated crystalline silicate, and a phosphorus modified zeolite.

In "Catalysts and conditions for the highly efficient, selective and stable heterogeneous oligomerisation of ethylene", J. Heveling, C.P. Nicolaides, M.S. Scurrall, Applied Catalysis A: General 173 (1998), 1-9, the oligomerisation of ethylene using a heterogeneous nickel catalyst is disclosed for the preparation of products in the C₄-C₂₀ range and present a characterization of a straight-run diesel product obtained from ethylene.

There remains a need in the art for processes which are effective for the production of liquid heavy hydrocarbon compositions, wherein the liquid heavy hydrocarbon composition comprises paraffinic hydrocarbons which boil above the C₂₂ mono-olefin boiling range.

In a first aspect, the present invention provides a process for the preparation of a liquid heavy hydrocarbon composition from ethylene, wherein said process comprises the following steps:

- (a) feeding an ethylene composition in to an oligomerisation reaction zone containing a supported nickel oligomerisation catalyst to form an oligomerisation product A, wherein the oligomerisation reaction is operated at a temperature in the range of from 30 to 300 °C and a pressure of at least 10 bara;
- (b) separating a light products stream B, a middle distillate product stream C and a heavy products stream D from oligomerisation product A, wherein the light product stream B comprises the fraction of oligomerisation product A which boils in the C₂-C₈ mono-olefin boiling range, the middle distillate product stream C comprises a fraction of oligomerisation product A which boils above the boiling range of the light product stream B and below the boiling range of the heavy products stream D, and wherein the heavy product stream D comprises the fraction of oligomerisation

product A which boils above the C22 mono-olefin boiling range;

- (c) recycling at least a portion of the light products stream B to the oligomerisation reaction zone of step (a) of the process;
- (d) optionally recycling at least a portion of the middle distillate product stream C to the oligomerisation reaction zone of step (a) of the process; and
- (e) hydrogenating the heavy products stream D,

wherein at least a portion of the hydrogenated heavy products stream D is recovered as the liquid heavy hydrocarbon composition.

In one particular embodiment of the present invention, the ethylene may be derived from the dehydration of ethanol.

Thus, in another aspect of the present invention, there is provided a process for the preparation of a liquid heavy hydrocarbon composition from ethanol, wherein said process comprises the following steps:

- (1) feeding an ethanol composition to a dehydration reactor containing an ethanol dehydration catalyst, wherein the dehydration reactor is operated at a temperature and pressure effective to dehydrate at least part of the ethanol to ethylene and water;
- (2) separating a stream comprising ethylene from the effluent of the dehydration reactor of step (1);
- (3) subjecting the stream comprising ethylene from step (2) to a process for removing any water, alcohols or other oxygenates which may be present; and
- (4) preparing the liquid heavy hydrocarbon composition from the ethylene stream from step (3) in accordance with a process for the preparation of a liquid heavy hydrocarbon composition as described herein.

The present invention also provides the use of a liquid heavy hydrocarbon composition prepared in accordance with a process for the preparation of a liquid heavy hydrocarbon composition as described herein as a base oil or base stock.

The present invention also provides a base oil or base stock comprising a liquid heavy hydrocarbon composition prepared in accordance with a process for the preparation of a liquid heavy hydrocarbon composition as described herein.

The present invention also provides a lubricating oil composition comprising a liquid

heavy hydrocarbon composition prepared in accordance with a process for the preparation of a liquid heavy hydrocarbon composition as described herein.

The present invention also provides the use of a liquid heavy hydrocarbon composition prepared in accordance with a process for the preparation of a liquid heavy hydrocarbon composition as described herein as a fuel oil.

The present invention also provides a fuel oil comprising a liquid heavy hydrocarbon composition prepared in accordance with a process for the preparation of a liquid heavy hydrocarbon composition as described herein.

In the process of the present invention, ethylene is fed to an oligomerisation reaction zone containing a supported nickel oligomerisation catalyst to form an oligomerisation product stream A, wherein the oligomerisation reaction zone is operating at a temperature in the range of from 30 to 300 °C and a pressure of at least 10 bara.

By the term “supported nickel oligomerisation catalyst”, it is meant a solid catalyst comprising nickel and at least one catalyst support, wherein the method of forming the catalyst is not limited and may include any method which results in a solid catalyst comprising a solid catalyst support and nickel.

The supported nickel oligomerisation catalyst contained within the oligomerisation reaction zone can be any supported nickel catalyst which is capable of oligomerising ethylene under at a temperature in the range of from 30 to 300 °C and at a pressure of at least 10 bara.

Preferably, the support for the oligomerisation catalyst comprises at least one porous material comprising silicon, aluminium and oxygen; examples of suitable porous material comprising silicon, aluminium and oxygen include amorphous silica-alumina and zeolites. More preferably, the support for the oligomerisation catalyst is based on at least one material selected from amorphous silica-alumina, zeolites or mixtures thereof.

In one particular embodiment, the support for the oligomerisation catalyst is selected from amorphous silica-alumina or a zeolite, with amorphous silica-alumina being preferred.

The supported nickel oligomerisation catalyst may be formed by any means of preparation of such catalysts known in the art. Examples suitable methods of preparing the supported nickel oligomerisation catalyst include impregnation, ion exchange and coprecipitation.

In one embodiment, the supported nickel oligomerisation catalyst is formed by impregnation of a nickel compound on a support, followed by drying and calcination of the impregnated support. The drying and calcination of the impregnated support may occur in a single step or as two or more separate steps. Typically, the nickel compound used for the preparation of the supported nickel oligomerisation catalyst by impregnation will be a soluble nickel salt.

In another embodiment, the supported nickel oligomerisation catalyst is formed by ion exchange of a nickel ion on to a support, followed by drying and calcining the ion-exchanged support. The drying and calcination of the ion-exchanged support may occur simultaneously or as two or more separate steps. The support used for the preparation of the supported nickel oligomerisation catalyst by ion-exchange will contain suitable sites which are capable of being ion-exchanged with a nickel ion. Suitable examples include zeolites and amorphous silica-alumina, in particular in either the acidic form or in the ammonium form.

In a further embodiment, the supported nickel oligomerisation catalyst can be prepared by coprecipitation of the nickel with the support material, such as described in, for example, US 5,849,972, the contents of which are incorporated herein by reference. The composition formed by coprecipitation will be dried and calcined prior to use as a supported nickel oligomerisation catalyst. The drying and calcination of the composition formed by coprecipitation may occur as a single step or as two or more separate steps.

Methods of impregnation, ion-exchange and coprecipitation would be known to a person skilled in the art.

The type of nickel compound used in the formation of the supported nickel oligomerisation catalyst is not limited, provided that it is suitable for use in the method of preparation employed. Typically, the nickel will be a soluble nickel salt or nickel complex. Examples of suitable nickel compounds which may be used in the preparation of the supported nickel oligomerisation catalyst include the nickel nitrate salts, nickel sulphate salts, nickel acetate salts, and mixtures thereof.

In one particular embodiment, the supported nickel oligomerisation catalyst comprises at least 0.1 wt% nickel, based upon the weight of the dry catalyst, preferably at least 0.2 wt% nickel, more preferably at least 0.3 wt% nickel, even more preferably at least 0.4 wt% nickel; in this embodiment, the supported nickel oligomerisation catalyst also

comprises at most 50 wt% nickel, based upon the weight of the dried catalyst, preferably at most 40 wt% nickel, more preferably at most 30 wt% nickel, even more preferably at most 20 wt% nickel. Specific examples according to this embodiment include supported nickel oligomerisation catalysts comprising from 0.1 to 50 wt% nickel, 0.1 to 50 wt% nickel, 0.2 to 50 wt% nickel, 0.3 to 50 wt% nickel, 0.4 to 50 wt% nickel, 0.1 to 40 wt% nickel, 0.2 to 40 wt% nickel, 0.3 to 40 wt% nickel, 0.4 to 40 wt% nickel, 0.1 to 30 wt% nickel, 0.2 to 30 wt% nickel, 0.3 to 30 wt% nickel, 0.4 to 30 wt% nickel, 0.1 to 20 wt% nickel, 0.2 to 20 wt% nickel, 0.3 to 20 wt% nickel and 0.4 to 20 wt% nickel, based upon the total weight of the dry catalyst.

In the embodiments wherein the catalyst is formed by impregnation or by ion exchange, the supported nickel oligomerisation catalyst preferably comprises from 0.1 to 10 wt% nickel, based upon the weight of the dried catalyst, preferably at least 0.2 to 8 wt% nickel, more preferably at least 0.3 to 6 wt% nickel.

In the embodiments wherein the catalyst is formed by coprecipitation, the supported nickel oligomerisation catalyst preferably comprises from 0.1 to 50 wt% nickel, based upon the weight of the dried catalyst, preferably from 0.2 to 40 wt% nickel, more preferably at least 0.3 to 30 wt% nickel, even more preferably from 0.4 to 20 wt% nickel.

In the embodiment wherein the nickel is impregnated on to the support, it is typically impregnated on to the support in the form of soluble nickel compound, such as a salt or complex. Suitable nickel compounds and solvents will be known to one skilled in the art. Examples of suitable nickel compounds include nickel nitrates, nickel acetates, nickel sulphates, nickel sulphonates, nickel phosphates, nickel phosphonates, nickel chloride, nickel bromide, nickel carbonate, nickel perchlorates, and mixtures thereof.. Examples of suitable solvents include water, methanol, ethanol, dimethyl ether, diethyl ether, and mixtures thereof; preferably, the solvent is selected from water, ethanol and mixtures thereof, more preferably water. The impregnated support is then washed, dried and calcined to form the supported nickel oligomerisation catalyst.

In the embodiment wherein the nickel is ion exchanged on to the support, the nickel is in the form of soluble cationic nickel compound, such as a nickel salt or cationic nickel complex, wherein a solution containing the cationic nickel compound is refluxed with the support for sufficient time such that at least a portion of the cationic sites on the support have been ion exchanged with the nickel cation. Examples of suitable nickel compounds

include nickel nitrates, nickel acetates, nickel sulphates, nickel sulphonates, nickel phosphates, nickel phosphonates, nickel chloride, nickel bromide, nickel carbonate, nickel perchlorates, and mixtures thereof. Examples of suitable solvents include water, methanol, ethanol, dimethyl ether, diethyl ether, and mixtures thereof; preferably, the solvent is selected from water, ethanol and mixtures thereof, more preferably water. The ion-exchanged support is then washed, dried and calcined to form the supported nickel oligomerisation catalyst.

In the embodiment wherein the supported nickel oligomerisation catalyst is prepared by coprecipitation, it is prepared by any suitable coprecipitation method known to one skilled in the art. In one example of this embodiment, the nickel is in the form of soluble nickel salt, wherein a solution of the nickel salt is admixed with a solution of the soluble aluminium compound, such as a salt, to form a solution comprising dissolved nickel and aluminium salts; the solution comprising dissolved nickel and aluminium salts is then admixed with an alkali metal waterglass solution, such as a sodium waterglass, at essentially constant pH and mixing. The desired coprecipitated composition forms a solid suspension in the solution, which is then filtered and washed until it is free of salts. Examples of suitable nickel salts include nickel nitrates, nickel acetates and nickel sulphates; examples of suitable aluminium salts include aluminium nitrates, aluminium acetates and aluminium sulphates. Typically the solvent used is water. The catalyst formed by coprecipitation is then washed, dried and calcined to form the supported nickel oligomerisation catalyst.

If the supported nickel oligomerisation catalyst prepared is not in the form of shaped particles, it may be formed into shaped particles, optionally with a binder, prior to use, for example by pelletisation or extrusion. If the catalyst is formed into shaped particles, then the shaped particles are typically dried and calcined prior to use in the oligomerisation process of the present invention. Alternatively, the supported nickel oligomerisation catalyst may be used in the form of a powder.

The oligomerisation reaction zone comprises at least one oligomerisation reactor. In one particular embodiment, the oligomerisation reaction zone comprises one oligomerisation reactor. In another particular embodiment, the oligomerisation zone comprises two or more reactors, said reactors being connected either in series, in parallel, or in combinations thereof.

The type of reactor used for the oligomerisation reaction zone is not limited.

Suitable types of reactors which may be used in the oligomerisation process of the present invention include fixed bed reactors, slurry bed reactors and bubble column reactors.

The oligomerisation reaction zone of step (a) is operated at a temperature in the range of from 50 to 300 °C, preferably at a temperature in the range of from 50 to 250 °C and more preferably a temperature in the range of from 100 to 200 °C.

The oligomerisation reaction zone of step (a) is operated at a pressure of at least 10 bara, preferably at a pressure in the range of from 10 to 100 bara and more preferably a pressure in the range of from 30 to 70 bara, such as, for example, in the range of from 50 to 70 bara.

The rate, in terms of mass hourly space velocity (MHSV), calculated as kg ethylene per kg dry catalyst per hour, at which the ethylene is fed to the oligomerisation reaction zone is preferably in the range of from 0.01 to 20 h⁻¹, more preferably from 0.05 to 15 h⁻¹, even more preferably from 0.1 to 10 h⁻¹.

The ethylene which is fed to the oligomerisation reaction zone may optionally contain other components which do not act as a catalyst poison or otherwise interfere with the supported nickel oligomerisation catalyst, such as diluents and/or solvents. Suitable diluents which may be included include nitrogen and other inert gases, such as the noble gases and gaseous alkanes. Suitable solvents which may be used include inert hydrocarbons, such as alkanes and naphthenes. In the embodiment where a solvent is used, the solvent may be an alkane or naphthene which boils within the boiling point range of the light products stream B and thus gets recycled back to the oligomerisation reaction zone in step (c) of the process; alternatively, the solvent may be an alkane or naphthene which boils above the boiling point range of the light products stream B and forms part of the middle distillate product stream C and/or the heavy products stream D prepared in the process of the present invention.

Depending upon the source of the ethylene, the ethylene which is fed to the oligomerisation reaction zone may also optionally contain other olefinic components. In one embodiment, the amount of olefins having three or more carbon atoms present in the ethylene which is fed to the oligomerisation reaction zone is at most 20 mol%, preferably at most 15 mol%, more preferably at most 10 mol%.

The water content of the total feed to the oligomerisation reaction zone is typically kept as low as possible; wherein the total feed to the oligomerisation reaction zone is the

total amount of all feed streams, e.g. ethylene, recycled streams, and any optional inert and/or solvent streams, that are fed to oligomerisation reaction zone. Preferably, the water content of the total feed to the oligomerisation reaction zone is at most 0.1 wt%, more preferably it is at most 0.01 wt%, and even more preferably at most 0.001 wt%, for example having at most 100 ppb by weight water, 10 ppb by weight water, 1 ppb by weight water, or having no detectable water content.

The source of the ethylene used in the process of the present invention is not limited and any available source of ethylene may be used.

In one embodiment the ethylene is derived from a hydrocarbon source, for example by pyrolysis of hydrocarbons, such as natural gas or naphtha, or by steam cracking of hydrocarbons, such as naphtha.

In another embodiment of the present invention, the ethylene may be derived from a “methanol to olefin” process, wherein methanol or dimethyl ether is subjected to a dehydration process to produce an olefinic product composition.

In another embodiment of the present invention, the ethylene may be derived from the dehydration of ethanol. In this embodiment, the ethanol may be derived from any known synthetic source or it may be a bioethanol. In the embodiment of the present invention wherein the ethylene is derived from the dehydration of bioethanol, the process of the present invention may be used to prepare a biomass derived liquid heavy hydrocarbon composition which may be used in base oils, lubricants and/or fuel oils.

Thus, in one particular aspect of the present invention, the ethylene used in the preparation of the liquid heavy hydrocarbon composition is derived from ethanol by a process which comprises the following steps:

- (1) feeding an ethanol composition to a dehydration reactor containing an ethanol dehydration catalyst, wherein the dehydration reactor is operated at a temperature and pressure effective to dehydrate at least part of the ethanol to ethylene and water;
- (2) separating a stream comprising ethylene from the effluent of the dehydration reactor of step (1);
- (3) subjecting the stream comprising ethylene from step (2) to a process for removing any water, alcohols or other oxygenates which may be present;

wherein the ethylene stream of step (3) is used as the source of ethylene in the preparation

of a heavy distillate hydrocarbon composition in accordance with a process as described herein.

In the embodiment wherein the ethylene is produced by the dehydration of bioethanol, the bioethanol is produced from a biological source, for example by fermentation of biomass and/or a derivative thereof. The term "biomass" as used herein refers to any biological source of a carbohydrate which may be converted to ethanol by fermentation of the biomass directly or fermentation of a derivative of the biomass; for example biological sources of sugars, starches and cellulose. For instance, bioethanol may be obtained by fermentation of feedstocks derived from sugar cane, such as sugar cane molasses and sugar cane juice; sugar beet, such as sugar beet molasses and sugar beet juice; cereal crops, such as corn or wheat derived feedstocks like corn syrup; and lignocellulosic materials, such as fast growing grasses or "energy grasses".

Alternatively, the ethanol may be derived from a fermentation process performed on a feed stream comprising carbon monoxide and hydrogen, such as synthesis gas. Such processes are described in, for example, WO 2012/062633 A1, the fermentation process described therein being incorporated herein by reference.

In the embodiment wherein the ethylene which is fed to the oligomerisation reaction zone is derived from the dehydration of ethanol, the ethanol composition which is fed to the dehydration reactor contains at least 50 wt% ethanol, more preferably at least 70 wt% ethanol, even more preferably at least 80 wt% ethanol, for example at least 90 wt%, provided that such other compounds would not adversely affect the dehydration catalyst or otherwise negatively impact on the dehydration process by, for example, reacting with the ethylene produced under the dehydration conditions or reacting with the ethanol under the dehydration conditions. In one particular embodiment, the ethanol composition is a hydrous ethanol composition. Such hydrous ethanol compositions may be the raw or crude ethanol composition which is resultant from the distillation of an ethanol product which has been obtained by the fermentation of biomass without further subjecting the obtained ethanol to a dewatering step. Such hydrous ethanol compositions may contain an amount of water which is equal to or greater than the amount of water which is determined by the azeotrope of the ethanol water composition produced during the fermentation process. Preferably, the ethanol composition which is fed to the dehydration reactor comprises less than 5 wt% of compounds other than ethanol, diethyl ether or water, preferably less than

2 wt% of compounds other than ethanol, diethyl ether or water, more preferably less than 1 wt% of compounds other than ethanol, diethyl ether or water.

Depending upon the source of ethanol, it may be desirable to subjecting to a purification step prior to feeding to the dehydration reactor; in particular, it has been observed that certain impurities which may be present in bioethanol, such as certain cationic, anionic, acidic, basic or nitrogenous impurities may negatively impact on the performance and/or life of the dehydration catalyst. Therefore, in one particular embodiment, the ethanol composition is subjected to a purification stage prior to being fed to the dehydration reactor, where the ethanol composition is a bioethanol composition; it is preferable that said bioethanol composition is first subjected to a purification stage prior to being fed to the dehydration reactor.

Examples of impurities which it may be desirable to remove from the ethanol composition prior to feeding to the dehydration reactor include nitrogen-containing contaminants, such as nitriles, amines, ammonium cations, amides, imides and heterocyclic nitrogen-containing compounds, aldehydes, ketones, carboxylic acids, carboxylic esters, and thio-compounds.

Thus, in one embodiment wherein the ethylene which is fed to the oligomerisation reaction zone is derived from the dehydration of ethanol, the ethanol composition is subjected to a purification stage in order to reduce the amount of impurities which are present in the ethanol composition. The purification stage may be implemented by means that are known to one skilled in the art, such as, for example, the use of at least one resin, the adsorption of impurities in/on a solid that is selected from among the molecular sieves, active carbon, alumina, aluminosilicates including zeolites, silica-aluminas and silicates, and distillation. Depending upon the nature of the impurities present, a further pretreatment stage may also be employed, such as a hydrogenation stage performed on the ethanol composition to hydrogenate any multiple bonds between carbon atoms and carbon atoms and any heteroatoms which may be present in any compounds in the ethanol composition, in the presence of a nickel-based catalyst, whereby said pretreatment stage is carried out before or after said purification stage.

The ethanol dehydration catalyst in the dehydration reactor of step (1) may be any of the ethanol dehydration catalysts that are known in the art. For example, the ethanol dehydration catalyst may be a crystalline silicate, a dealuminated crystalline silicate or a

phosphorus modified zeolite as described in WO 2009/098262, the contents of which are incorporated herein by reference. Alternatively, the ethanol dehydration catalyst may be a heteropolyacid catalyst, for instance as described by WO 2008/138775 and WO 2008/062157, the contents of which are incorporated herein by reference. In preferred
5 embodiments, the ethanol dehydration catalyst is a heteropolyacid catalyst. The heteropolyacid catalyst is preferably supported on a suitable inert support, such as silica or alumina.

Suitable conditions for dehydrating alcohols are known in the art and would be known to the skilled person, for instance with reference to the prior art documents cited
10 herein. However, in the case of a crystalline silicate or zeolite alcohol dehydration catalyst, typical reaction conditions include a temperature of from 280 to 500 °C, a total pressure of from 0.5 to 30 bara, and a partial pressure of ethanol that is preferably from 1.2 to 4 bara. In the case of a heteropolyacid catalyst, typical reaction conditions include a temperature of from 180 to 270 °C and a pressure of from 1 to 45 bara.

15 Preferably, the ethanol composition is fed to the dehydration reactor in the vapour phase.

The effluent from the dehydration reactor comprises at least ethylene and water, and may also comprise unreacted ethanol and diethyl ether by-product, both of which may conveniently be recycled back to the dehydration reactor.

20 The separation of an ethylene stream from the dehydration reactor effluent may be achieved by any means known in the art, such as flash separation.

Prior to feeding the ethylene stream to the oligomerisation reaction zone, it may be desirable to subject the ethylene stream to a process for removing any water, alcohols or other oxygenates which may be present therein; by the term other oxygenates used herein,
25 it is meant any compound in the effluent which contains at least one oxygen atom, such as, for instance, diethyl ether, acetaldehyde, ethyl acetate, carbon monoxide and carbon dioxide. The removal of any water, alcohols or other oxygenates which may be present may conveniently be achieved by any process or combination of processes known in the art.

30 In one embodiment, the process for removing any water, alcohols or other oxygenates which may be present is achieved by passing the ethylene stream through a suitable guard bed or guard beds. Molecular sieve 3A is a well-known material which is

suitable for use in removing water from an ethylene stream and may be used as a guard bed to remove at least water from an ethylene stream.

In another embodiment, the process for removing any water, alcohols or other oxygenates which may be present is achieved by one or more distillation processes.

5 In another embodiment, the ethylene may comprise a mixture of ethylene which has been derived from two or more sources; such as a mixture of ethylene which has been derived from the cracking of a hydrocarbon source and ethylene which has been derived from the dehydration of ethanol.

The oligomerisation product stream A formed in the oligomerisation reaction zone of
10 step (a) consists of any unreacted ethylene, any diluents or solvents fed to or present in the oligomerisation reaction zone, and products of the oligomerisation reaction zone. The products of the oligomerisation reaction zone comprises a mixture of straight and branched chain olefins, wherein said olefins comprise a mixture of both alpha-olefins and internal olefins, with the majority of the oligomerisation products having an even number of carbon
15 atoms. The distribution of carbon numbers in the oligomerisation products will be dependent upon the nature and amount of light products stream B that is recycled to the oligomerisation reaction zone, and in the embodiments wherein at least part of the middle distillate products stream C is recycled, the distribution of carbon numbers in the oligomerisation products will additionally be dependent upon the nature and amount of
20 middle distillate products stream C that is recycled to the oligomerisation reaction zone. In one embodiment, the proportion of internal olefins in the oligomerisation products increase with increasing carbon chain length and/or the proportion of branched compounds in the oligomerisation products increase with increasing carbon chain length. In one embodiment, the fraction of the oligomerisation products which boils above the light
25 products stream B comprises greater than 50 mol% internal olefins.

In step (b) of the process, a light products stream B, a middle distillate product stream C and a heavy products stream D are separated from oligomerisation product A, wherein the light product stream B comprises the fraction of oligomerisation product A which boils in the C2-C8 mono-olefin boiling range, the middle distillate product stream C
30 consists of a fraction of oligomerisation product A which boils above the boiling range of the light product stream B and below the boiling range of the heavy products stream D, and the heavy product stream D comprises the fraction of oligomerisation product A which

boils above the C22 mono-olefin boiling range. By the term “mono-olefin boiling range” it is meant the boiling points of the olefin compositions having the empirical formula C_xH_{2x} , for example the C8 mono-olefin boiling range is the boiling range of olefins having the empirical formula C_8H_{16} .

5 Optionally, at least a portion of the middle distillate product stream C may be recovered as a separate middle distillate hydrocarbon product composition. If at least a portion of the middle distillate product stream C is to be recovered as a separate middle distillate hydrocarbon product composition, said middle distillate product stream C may optionally be subjected to a hydrogenation process to reduce or remove the level of
10 unsaturation therein.

 In one embodiment, the light products stream B consists of the fraction of oligomerisation product stream A which boils in the C2-C8 mono-olefin boiling range. However, in the embodiments wherein at least a portion of the remaining middle distillate product stream C from step (c) is recovered as a middle distillate hydrocarbon
15 composition, the light products stream B may consist of the fraction of oligomerisation product stream A which boils below the lowest boiling point of the middle distillate hydrocarbon composition which is to be recovered.

 Any components in the oligomerisation product A which may be present and have a boiling point below the boiling point of ethylene ($-103.7\text{ }^{\circ}\text{C}$ at atmospheric pressure
20 (1.013 bar)) may also be included in the light products fraction. To prevent build-up of any components having a boiling point below the boiling point of ethylene or any inert compounds, such as alkanes, in the oligomerisation process, part of light products stream B may be purged during the step of recycling at least part of the light products stream B.

 In one embodiment of the present invention, the light products stream B boils below
25 $130\text{ }^{\circ}\text{C}$ at atmospheric pressure (at 1.013 bar). In another embodiment of the present invention, the light products stream B boils in the range of from $-105\text{ }^{\circ}\text{C}$ to $130\text{ }^{\circ}\text{C}$, in particular in the range of from $-103.7\text{ }^{\circ}\text{C}$ to $130\text{ }^{\circ}\text{C}$, at atmospheric pressure (at 1.013 bar). In another embodiment of the present invention, the light products stream B boils below
30 $140\text{ }^{\circ}\text{C}$ at atmospheric pressure (at 1.013 bar). In another embodiment of the present invention, the light products stream B boils in the range of from $-105\text{ }^{\circ}\text{C}$ to $140\text{ }^{\circ}\text{C}$, in particular in the range of from $-103.7\text{ }^{\circ}\text{C}$ to $140\text{ }^{\circ}\text{C}$, at atmospheric pressure (at 1.013 bar). In another embodiment of the present invention, the light products stream B boils below

150 °C at atmospheric pressure (at 1.013 bar). In another embodiment of the present invention, the light products stream B boils in the range of from -105 °C to 150 °C, in particular in the range of from -103.7 °C to 150 °C, at atmospheric pressure (at 1.013 bar). In another embodiment of the present invention, the light products stream B boils below
5 160 °C at atmospheric pressure (at 1.013 bar). In another embodiment of the present invention, the light products stream B boils in the range of from -105 °C to 160 °C, in particular in the range of from -103.7 °C to 160 °C, at atmospheric pressure (at 1.013 bar). In another embodiment of the present invention, the light products stream B boils below
10 170 °C at atmospheric pressure (at 1.013 bar). In another embodiment of the present invention, the light products stream B boils in the range of from -105 °C to 170 °C, in particular in the range of from -103.7 °C to 170 °C, at atmospheric pressure (at 1.013 bar).

The middle distillate product stream C will comprise of at least part of the fraction of oligomerisation product A that boils above the boiling range of the light product stream B and below the boiling range of the heavy products stream D. In one particular embodiment
15 of the present invention, the middle distillate product stream C will comprise the entire fraction of oligomerisation product A that boils above the boiling range of the light product stream B and below the boiling range of the heavy products stream D.

The heavy products stream D comprises the fraction of oligomerisation product A which boils above the C22 mono-olefin boiling range. Depending on the desired use of the
20 liquid heavy hydrocarbon composition, the lower boiling point limit of the heavy products stream D may be below than the C22 mono-olefin boiling range, in such circumstances the heavy products stream will comprise the fraction of the oligomerisation product A which boils above a lower boiling point limit desired for the desired use of the liquid heavy hydrocarbon composition. Alternatively, in the embodiments wherein at least a portion of
25 the remaining middle distillate product stream C from step (c) is recovered as a middle distillate hydrocarbon composition, the lower boiling point limit of the heavy products stream D may conveniently be determined by the desired upper boiling point of the middle distillate product stream C; thus, depending upon the desired composition of the middle distillate hydrocarbon composition, the heavy products stream D may consist of the
30 fraction of oligomerisation product A which boils above the C22 mono-olefin boiling range, alternatively, the heavy products stream D may consist of the fraction of oligomerisation product A which boils above a temperature selected from 350 °C, 330 °C,

320 °C, 310 °C, 290 °C, 280 °C, 270 °C, 260 °C and 250 °C. In another particular embodiment, the heavy product stream D comprises the fraction of oligomerisation product A which boils above the Diesel fuel boiling range. In yet another particular embodiment, the heavy product stream D comprises the fraction of the oligomerisation product A which
5 boils above the jet fuel boiling range.

The middle distillate products stream C comprises a fraction of the oligomerisation product A which has a lower boiling point which is above the C8 mono-olefin boiling point range and an upper boiling point which is up to the C22 mono-olefin boiling point range. In another embodiment, the middle distillate products stream C contains the
10 fraction of the oligomerisation product A which boils in the temperature range have a lower limit selected from any one of the following: 130 °C, 140 °C, 150 °C, 160 °C, 170 °C, 180 °C, 200 °C, 220 °C and 250 °C; and an upper limit selected from any one of the following: 350 °C, 330 °C, 320 °C, 310 °C, 290 °C, 280 °C, 270 °C, 260 °C and 250 °C; with the proviso that there is at least a 10 °C difference between the lower and
15 upper limit in the temperature range.

In one embodiment of the present invention, the light products stream B will consist of the fraction which is separated in step (b) of the process which has boiling point lower than the boiling point range of the middle distillate products stream C, and the heavy products stream D will consist of the fraction which is separated in step (b) of the process
20 which has boiling point higher than the boiling point range of the middle distillate products stream C. Thus, in one embodiment of the present invention, the separation of the light products stream B, the middle distillate products stream C and the heavy products stream D in step (b) will be performed such that the upper boiling point limit of the lights product stream B will be the same as the lower boiling point limit of the middle distillate products
25 stream C and the lower boiling point limit of the heavy products stream D will be the same as the upper boiling point limit of the middle distillate products stream C.

It will be understood by a skilled person that due to the process of fractionation of hydrocarbon streams, such as those produced in the process of the present invention, may result in small amounts of hydrocarbon compounds having boiling points outside of the
30 range selected; for instance, whilst a distillation column or flash vessel may be operated to separate a hydrocarbon stream in to a lighter fraction having a boiling point of at most 180 °C and a heavier fraction having a boiling point of at least 180 °C, the lighter fraction

may contain small amounts hydrocarbon compounds which have a boiling point greater than 180 °C and the heavier fraction may contain small amounts hydrocarbon compounds which have a boiling point lower than 180 °C. Thus, when referring to upper boiling points, lower boiling points and boiling point ranges in the present invention, it is meant
5 that at least 90 wt%, preferably at least 95 wt%, of the fraction boils above the specified lower boiling point limit and/or below the specified upper boiling point limit, or at least 80 wt%, preferably at least 90 wt%, of the fraction boils within the specified boiling point range.

The means of separation of the light products stream B, the middle distillate products
10 stream C and the heavy products stream D, in step (b), is not limited. In one embodiment of the present invention, the separation performed in step (b) is performed in a single distillation column. In another embodiment of the present invention, the separation performed in step (b) is performed in a series of two or more distillation columns. In another embodiment of the present invention, the separation performed in step (b) is
15 performed in a series of two or more flash distillation vessels. In another embodiment of the present invention, the separation performed in step (b) is performed in a system which comprises at least one flash distillation vessel and at least one distillation column.

Thus, in a specific embodiment of the process of the present invention, step (b) is performed in a single distillation column with a three effluent streams: light products
20 stream B, middle distillate products stream C and heavy products stream D.

In another specific embodiment of the process of the present invention, step (b) is performed by a process comprising at least the following steps:

- (i) separating the light products stream B from the oligomerisation product A to produce a combined middle distillate and heavy stream G, and
25 (ii) separating the middle distillate product stream C and the heavy products stream D from the combined middle distillate and heavy stream G.

The means of separation for each of steps (i) and (ii) of this process are not limited, and each step may be performed in one or more distillation columns and/or flash distillation vessels.

Thus, when step (b) of the process of the present invention is performed by a process
30 comprising at least steps (i) and (ii) as described above, the overall process for the preparation of a liquid heavy hydrocarbon composition from ethylene comprises the

following steps:

- (a) feeding an ethylene composition in to an oligomerisation reaction zone containing a supported nickel oligomerisation catalyst to form an oligomerisation product A, wherein the oligomerisation reaction is operated at a temperature in the range of from 30 to 300 °C and a pressure of at least 10 bara;
- (b-i) separating the light products stream B from the oligomerisation product A to produce a combined middle distillate and heavy stream G, wherein the light product stream B comprises the fraction of oligomerisation product A which boils in the C2-C8 mono-olefin boiling range and the combined middle distillate and heavy stream G comprises the fraction of oligomerisation product A which boils above the boiling range of the light product stream B;
- (b-ii) separating a middle distillate product stream C and a heavy products stream D from the combined middle distillate and heavy stream G, wherein the middle distillate product stream C comprises a fraction of the combined middle distillate and heavy stream G which boils below the boiling range of the heavy products stream D, and wherein the heavy product stream D comprises the fraction of the combined middle distillate and heavy stream G which boils above the C22 mono-olefin boiling range;
- (c) recycling at least a portion of the light products stream B to the oligomerisation reaction zone of step (a) of the process;
- (d) optionally recycling at least a portion of the middle distillate product stream C to the oligomerisation reaction zone of step (a) of the process; and
- (e) hydrogenating the heavy products stream C,
- wherein the at least a portion of the hydrogenated heavy products stream D is recovered as the liquid heavy hydrocarbon composition.

In the process of the present invention, the heavy product stream D is subjected to a hydrogenation process in order to reduce the level of olefinic unsaturation in the final liquid heavy hydrocarbon composition compared to the heavy product stream D or to remove the olefinic unsaturation in the liquid heavy hydrocarbon composition.

Therefore, in step (e) of the present invention, the heavy product stream D is hydrogenated by any known hydrogenation process. Typically, the hydrogenation process will comprise contacting the heavy product stream D with hydrogen-rich gas in the

presence of a suitable hydrogenation catalyst under hydrogenation reaction conditions.

Examples of suitable hydrogenation catalysts include catalysts based on Group VIII metals, in particular catalysts based on nickel, palladium, platinum, rhodium and ruthenium.

5 In one embodiment, the hydrogenation catalyst comprises a metal selected from palladium and nickel, on a support comprising alumina, silica or silica-alumina. In this embodiment, the metal content of the catalyst will typically be in the range of from 0.1 to 10 wt% for palladium and in the range of from 1 to 60 wt% for nickel. In this
10 embodiment, the operating conditions typically comprise a liquid hourly space velocity of from 1 to 8 h⁻¹, a temperature in the range of from 100 to 250 °C at the hydrogenation reactor inlet and a pressure of from 2 to 5 MPa.

The extent to which the heavy product stream D is hydrogenated will depend upon the desired use of the liquid heavy hydrocarbon composition.

In the embodiment wherein step (b) is performed by a process comprising at least
15 steps (i) and (ii) indicated herein, the combined middle distillate and heavy stream G may optionally be subjected to a hydrogenation process prior to step (ii). When the combined middle distillate and heavy stream G is subjected to a hydrogenation process, said stream may be hydrogenated by any known hydrogenation process. Typically, the hydrogenation
20 process will comprise contacting the combined middle distillate and heavy stream G with hydrogen-rich gas in the presence of a suitable hydrogenation catalyst under hydrogenation reaction conditions. Examples of suitable catalysts and process would be known to one skilled in the art, such as those processes described in relation to step (e), which are explicitly included in this embodiment.

In the embodiments wherein the separation of the heavy products stream D is
25 performed prior to a hydrogenation reaction being performed on the stream from which it is separated, whilst not essential, it is preferred to perform the separation of the heavy products stream D under reduced pressure.

In the embodiment wherein step (b) is performed by a process comprising at least steps (i) and (ii) indicated herein, the hydrogenation of the heavy product stream D
30 (referred to as step (e) in the first embodiment of the invention) may be performed on the heavy product stream D prior to the separation of the middle distillate product stream C and the heavy product stream D in step (ii); namely, the hydrogenation step is performed

on the combined middle distillate and heavy stream G.

Therefore, in one particular embodiment of the present invention there is provided a process for the preparation of a liquid heavy hydrocarbon composition from ethylene comprises the following steps:

- 5 (a) feeding an ethylene composition in to an oligomerisation reaction zone containing a supported nickel oligomerisation catalyst to form an oligomerisation product A, wherein the oligomerisation reaction is operated at a temperature in the range of from 30 to 300 °C and a pressure of at least 10 bara;
 - (b-i) separating the light products stream B from the oligomerisation product A to
10 produce a combined middle distillate and heavy stream G, wherein the light product stream B comprises the fraction of oligomerisation product A which boils in the C2-C8 mono-olefin boiling range and the combined middle distillate and heavy stream G comprises the fraction of oligomerisation product A which boils above the boiling range of the light product stream B;
 - 15 (b-ii) hydrogenating the combined middle distillate and heavy stream G;
 - (b-iii) separating a hydrogenated middle distillate product stream C and a heavy products stream D from the combined middle distillate and heavy stream G, wherein the hydrogenated middle distillate product stream C comprises a fraction of the
20 combined middle distillate and heavy stream G which boils below the boiling range of the heavy products stream D, and wherein the heavy product stream D comprises the fraction of the combined middle distillate and heavy stream G which boils above the C22 mono-olefin boiling range;
 - (c) recycling at least a portion of the light products stream B to the oligomerisation reaction zone of step (a) of the process;
 - 25 (d) optionally recycling at least a portion of the middle distillate product stream C to the oligomerisation reaction zone of step (a) of the process; and
- wherein the at least a portion of the hydrogenated heavy products stream D is recovered as the liquid heavy hydrocarbon composition.

In the embodiments wherein the combined middle distillate and heavy stream G is
30 hydrogenated, it is preferred not to recycle any of the middle distillate product stream C to the oligomerisation reaction zone of step (a) of the process.

In the present invention, at least a portion of the light products stream B is recycled

back to the oligomerisation reaction zone of step (a) of the process. In one particular embodiment, all of the light products stream B is recycled back to the oligomerisation reaction zone of step (a) of the process; in this embodiment, the removal of a purge stream to prevent build-up of products boiling below the boiling point of ethylene and other unreactive or otherwise undesirable components is permissible. In another embodiment, part of the light products stream B is recycled back to the oligomerisation reaction zone of step (a) of the process and another part of the light products stream B is separated as a separate product composition. In yet a further embodiment, part of the light products stream B is recycled back to the oligomerisation reaction zone of step (a) of the process and another part of the light products stream B is separated and used as fuel to provide heat energy to one or more parts of the process or processes upstream or downstream of the process of the present invention; such as preheating and vapourising ethanol which is to be dehydrated or providing heat energy to a separation, cracking, hydrogenation or optional dehydration process.

Any components in the oligomerisation product A which may be present and have a boiling point below the boiling point of ethylene (-103.7°C at atmospheric pressure (1.013 bar)) will typically be included in the light products fraction. To prevent build-up of any components having a boiling point below the boiling point of ethylene or any inert compounds, such as alkanes, in the oligomerisation process, part of light products stream B may be purged during the step of recycling at least part of the light products stream B.

In step (d), at least a portion of the remaining middle distillate products stream C may optionally be recycled back to the oligomerisation reaction zone of step (a) of the process. In one particular embodiment, all of the remaining middle distillate products stream C is recycled back to the oligomerisation reaction zone of step (a) of the process. In another embodiment, part of the remaining middle distillate products stream C is recycled back to the oligomerisation reaction zone of step (a) of the process and another part of the remaining middle distillate products stream C is separated and recovered as a separate middle distillate hydrocarbon product composition. In another embodiment, there is no recycling of the remaining middle distillate products stream C to the oligomerisation reaction zone of step (a) of the process and all of the middle distillate products stream C is recovered as a separate middle distillate hydrocarbon product composition.

In the embodiments wherein the middle distillate product stream C is to be recycled

and said middle distillate product stream C has been separated from a combined middle distillate and heavy stream G which has been hydrogenated, such a middle distillate product stream C may optionally be subjected to a dehydrogenation process prior to recycling. Subjecting such a middle distillate product stream C to a dehydrogenation process is not essential to the process as non-olefinic hydrocarbons not be reactive in the oligomerisation reaction of step (a) of the process; however, it may be desirable to control build-up of non-olefinic hydrocarbons in the oligomerisation reaction zone through removal of a purge stream from the recycle stream of such a middle distillate product stream C.

In any of the embodiments wherein a stream is subject to a dehydrogenation reaction, the nature of the dehydrogenation reaction is not critical. Examples of suitable dehydrogenation reactions include catalytic dehydrogenation reactions using a dehydrogenation catalyst under suitable dehydrogenation reaction conditions. Suitable reactions and catalysts would be known to one skilled in the art.

In a first alternative process, the present invention provides a process for the preparation of a liquid heavy hydrocarbon composition from ethylene, wherein said process comprises the following steps:

(A) feeding an ethylene composition in to an oligomerisation reaction zone containing a supported nickel oligomerisation catalyst to form an oligomerisation product A, wherein the oligomerisation reaction is operated at a temperature in the range of from 30 to 300 °C and a pressure of at least 10 bara;

(B) separating a combined light and middle distillate product stream H and a heavy products stream D from oligomerisation product A, wherein the heavy product stream D comprises the fraction of oligomerisation product A which boils above the C22 mono-olefin boiling range and wherein the combined light and middle distillate product stream H consists of the fraction of oligomerisation product A which boils below the boiling range of the heavy products stream D;

(C) recycling at least a portion of the combined light and middle distillate product stream H to the oligomerisation reaction zone of step (A) of the process; and,

(D) hydrogenating the heavy products stream D,

wherein at least a portion of the hydrogenated heavy products stream D is recovered as the liquid heavy hydrocarbon composition.

The separation performed in step (B) of the first alternative process is preferably performed under reduced pressure.

In step (D) of the first alternative process, the heavy product stream D is subjected to a hydrogenation process in order to reduce the level of olefinic unsaturation in the final
5 liquid heavy hydrocarbon composition compared to the heavy product stream D or to remove the olefinic unsaturation in the liquid heavy hydrocarbon composition. Details of the catalysts and conditions for the hydrogenation process of step (D) of the first alternative process are the same as for step (e) of the first aspect of the present invention.

The liquid heavy hydrocarbon composition which is recovered from a process of the
10 present invention may be used directly as a base oil or base stock, fuel oil, or component thereof, or may be subjected to further fractionated or separated and a portion of the liquid heavy hydrocarbon composition is recovered and used as a base oil or base stock, fuel oil, or component thereof.

The liquid heavy hydrocarbon composition prepared by a process according to the
15 present invention will comprise paraffinic hydrocarbons which boil above the C22 mono-olefin boiling range. Additionally, lower boiling components may also be present in the liquid heavy hydrocarbon composition prepared by a process according to the present invention, for example, the liquid heavy hydrocarbon composition may comprise paraffinic hydrocarbons which boil above a temperature selected from 340 °C, 320 °C or 300 °C, at
20 atmospheric pressure.

The present invention also provides the use of a liquid heavy hydrocarbon composition prepared in accordance with a process for the preparation of a liquid heavy hydrocarbon composition as described herein as a base oil or base stock.

The present invention also provides a base oil or base stock comprising a liquid
25 heavy hydrocarbon composition prepared in accordance with a process for the preparation of a liquid heavy hydrocarbon composition as described herein.

The present invention also provides a lubricating oil composition comprising a liquid heavy hydrocarbon composition prepared in accordance with a process for the preparation of a liquid heavy hydrocarbon composition as described herein.

30 The present invention also provides the use of a liquid heavy hydrocarbon composition prepared in accordance with a process for the preparation of a liquid heavy hydrocarbon composition as described herein as a fuel oil.

The present invention also provides a fuel oil comprising a liquid heavy hydrocarbon composition prepared in accordance with a process for the preparation of a liquid heavy hydrocarbon composition as described herein.

Examples

5 Preparation of Catalyst

Davicat 3125 (Trade Mark) silica-alumina powder (50 g), supplied by Grace Davison, was weighed into a 500 mL round bottomed flask. A solution of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (9.51 g) in water (150 mL) was added, and the mixture refluxed for 4 hours with stirring. After cooling, the suspension was filtered and washed extensively with deionised water
10 using vacuum filtration. The resulting solid was dried in an oven at 110 °C for 18 hours. Analysis showed that the product contained 2.1 wt% nickel.

The catalysts used in the testing were of a 125-160 µm particle size. To form the catalysts of the specified particle size, the dried solid was pelletised using a KBr press (press force 10 t, tool diameter 13 mm); the pelletised solid was then crushed with a mortar
15 and pestle and pressed through a series of 1000 µm, 500 µm, 250 µm and finally through a 160 µm sieves. Shaking on a sieving device for 10 min at 70 Hz yielded the corresponding particle size fractions.

Catalyst testing

Two reactor tubes of 4.5 mm diameter were filled with an amount of catalyst
20 equivalent to a dry weight of (a) 0.5 g and (b) 0.25 g. The dry weight of the catalyst was determined by LOI (loss of ignition) tests at 300 °C.

The catalysts were activated by heating at 300 °C for 3 hours under pure N_2 (3.1 NL/h to each reactor) to purge the catalyst bed free from air and residual moisture. The reactor tube pressure was then set to 39 bar and temperature to 120 °C and a gas
25 mixture comprising 10.2 mol% Ar and 89.8 mol% dry C_2H_4 was passed through each reactor tube, such that the feed rates of the components of the mixture to each tube were 75 normal cm^3/hour for argon and 656 normal cm^3/hour for ethylene, where “normal cm^3/hour is the volume that would be used if the gases were at atmospheric pressure

For each reactor tube, the product stream leaving the reactor tube was mixed with
30 nitrogen and passed through a condenser vessel at 110 °C to collect liquid products. After 24 hours of operation the liquids were collected and analysed for olefin content. The gases leaving each reactor tube at this time were also analysed for olefin content. The data

shown in Figure 1 gives the combined analytical results as mass% of total hydrocarbon product for the gas and liquid streams.

The two reactor tubes contained the same catalyst, with 0.25 g and 0.5 g. Consequently, the analysis of the product from the reactor tube containing 0.25 g catalyst is an indication of the composition at the midpoint of the catalyst bed in the reactor tube containing 0.5 g catalyst. The product composition leaving the reactor tube with 0.5 g and the product composition at the midpoint of the catalyst bed allow the extent of reaction in the first and second halves of the catalyst bed to be compared.

Thus, at the midpoint of the catalyst bed, all of the ethylene feed has been consumed. In the second half of the catalyst bed, the concentration of C₄, C₆ and C₈ olefins decreases, while the concentration of heavier olefins increases. This indicates that at least the C₄, C₆ and C₈ olefins are reacted and converted into heavier olefins in the presence of the catalyst under the reaction conditions.

Claims

1. A process for the preparation of a liquid heavy hydrocarbon composition from ethylene, wherein said process comprises the following steps:

- 5 (a) feeding an ethylene composition in to an oligomerisation reaction zone containing a supported nickel oligomerisation catalyst to form an oligomerisation product A, wherein the oligomerisation reaction is operated at a temperature in the range of from 30 to 300 °C and a pressure of at least 10 bara;
- 10 (b) separating a light products stream B, a middle distillate product stream C and a heavy products stream D from oligomerisation product A, wherein the light product stream B comprises the fraction of oligomerisation product A which boils in the C2-C8 mono-olefin boiling range, the middle distillate product stream C comprises a fraction of oligomerisation product A which boils above the boiling range of the light product stream B and below the boiling range of the heavy products stream D,
- 15 and wherein the heavy product stream D comprises the fraction of oligomerisation product A which boils above the C22 mono-olefin boiling range;
- (c) recycling at least a portion of the light products stream B to the oligomerisation reaction zone of step (a) of the process;
- (d) optionally recycling at least a portion of the middle distillate product stream C to
- 20 the oligomerisation reaction zone of step (a) of the process; and
- (e) hydrogenating the heavy products stream C,
- wherein the at least a portion of the hydrogenated heavy products stream D is recovered as the liquid heavy hydrocarbon composition.

2. A process according to claim 1, wherein the separation of a light products stream B,

25 a middle distillate product stream C and a heavy products stream D from oligomerisation product A of step (b) is performed by a process comprising at least the following steps:

- (i) separating the light products stream B from the oligomerisation product A to produce a combined middle distillate and heavy stream G, and
- (ii) separation the middle distillate product stream C and the heavy products stream D
- 30 from the combined middle distillate and heavy stream G.

3. A process according to claim 2, wherein the combined middle distillate and heavy stream G is subjected to a hydrogenation process prior to step (ii).

4. A process according to claim 2, wherein the hydrogenation step (e) is performed on the combined middle distillate and heavy stream G prior to step (ii).

5. A process for the preparation of a liquid heavy hydrocarbon composition from ethylene, wherein said process comprises the following steps:

5 (A) feeding an ethylene composition in to an oligomerisation reaction zone containing a supported nickel oligomerisation catalyst to form an oligomerisation product A, wherein the oligomerisation reaction is operated at a temperature in the range of from 30 to 300 °C and a pressure of at least 10 bara;

10 (B) separating a combined light and middle distillate product stream H and a heavy products stream D from oligomerisation product A, wherein the heavy product stream D comprises the fraction of oligomerisation product A which boils above the C22 mono-olefin boiling range and wherein the combined light and middle distillate product stream H consists of the fraction of oligomerisation product A which boils below the boiling range of the heavy products stream D;

15 (C) recycling at least a portion of the combined light and middle distillate product stream H to the oligomerisation reaction zone of step (A) of the process; and,

(D) hydrogenating the heavy products stream C,
wherein the at least a portion of the hydrogenated heavy products stream D is recovered as the liquid heavy hydrocarbon composition.

20 6. A process according to any one of claims 1 to 5, wherein the oligomerisation catalyst comprises an amorphous silica-alumina support.

7. A process according to any one of claims 1 to 6, wherein the supported nickel oligomerisation catalyst comprises from 0.4 to 20 wt% nickel, based upon the total weight of the dry catalyst.

25 8. A process according to any one of claims 1 to 7, wherein the oligomerisation reaction is operated at a temperature in the range of from 50 to 250 °C.

9. A process according to any one of claims 1 to 8, wherein the oligomerisation reaction of step (a) is operated at a pressure in the range of from 10 to 100 bara.

30 10. A process for the preparation of a liquid heavy hydrocarbon composition from ethanol, wherein said process comprises the following steps:

(1) feeding an ethanol composition to a dehydration reactor containing an ethanol dehydration catalyst, wherein the dehydration reactor is operated at a temperature

and pressure effective to dehydrate at least part of the ethanol to ethylene and water;

(2) separating a stream comprising ethylene from the effluent of the dehydration reactor of step (1);

5 (3) subjecting the stream comprising ethylene from step (2) to a process for removing any water, alcohols or other oxygenates which may be present; and

(4) preparing the liquid heavy hydrocarbon composition from the ethylene stream from step (3) in accordance with the process of any one of claims 1 to 9.

10 11. Use of a liquid heavy hydrocarbon composition prepared in accordance with the process of any one of claims 1 to 10 as a base oil or base stock.

12. A base oil or base stock comprising a liquid heavy hydrocarbon composition prepared in accordance with the process of any one of claims 1 to 10.

13. A lubricating oil composition comprising a liquid heavy hydrocarbon composition prepared in accordance with the process of any one of claims 1 to 10.

15 14. Use of a liquid heavy hydrocarbon composition prepared in accordance with the process of any one of claims 1 to 10 as a fuel oil.

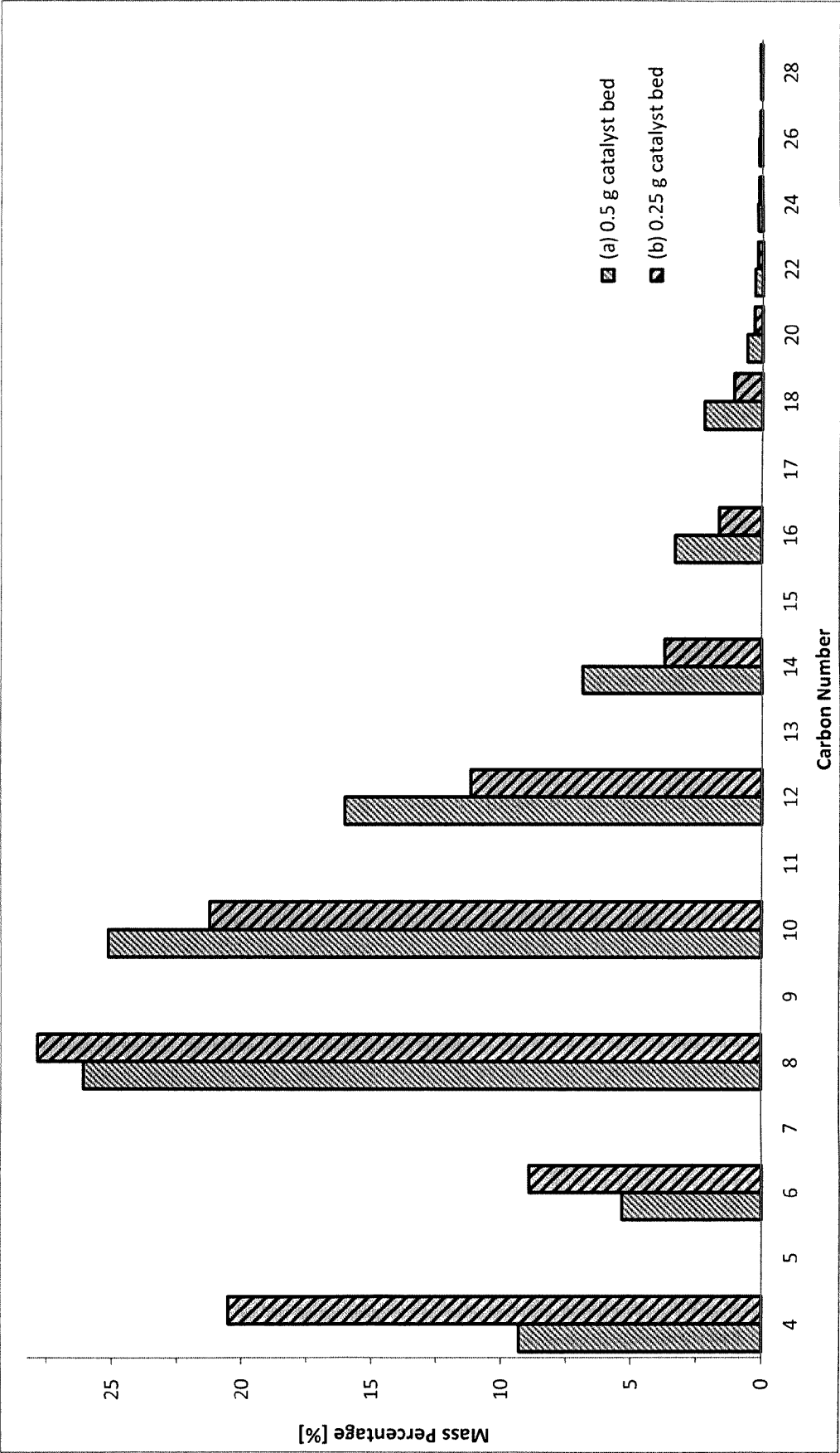
15. A fuel oil comprising a liquid heavy hydrocarbon composition prepared in accordance with the process of any one of claims 1 to 10.

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25

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Figure 1



INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2014/056153

A. CLASSIFICATION OF SUBJECT MATTER

INV. C10G29/20 C10G50/02 C10G69/12
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C10G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2012/039838 A2 (SYNFUELS INT INC [US]; CANTRELL JOEL [US]; MORROW DUANE [US]; PETERSON) 29 March 2012 (2012-03-29) paragraphs [0037] - [0038], [0040], [0041], [0058] - [0061], [0064] - [0066], [0069] - [0071], [0075] - [0076], [0133] - [0139] figures 1-16 figures 1-3	1-15
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Further documents are listed in the continuation of Box C.



See patent family annex.

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Date of the actual completion of the international search

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Date of mailing of the international search report

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INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2014/056153

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